Scanning Electron Microscopy Characterization of Domain Structures in Fast Ionic Conductor $Li_{3x}La_{2/3-x}TiO_3$

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The development of fast-ion conductors, known also as superionic conductors and solid-state electrolytes, is of increasing importance because of their potential application in supercapacitors, Li-ion batteries, solid-state fuel cells and electrochemical sensors. Conventional batteries for powering electrochemical devices with high energy and power densities contain organic liquid electrolytes, which require rigorous safety strategies and are thus inhibitively expensive for large-scale applications. All-solid-state batteries using nonflammable solid electrolytes offer significant advantages in terms of improved safety and chemical and thermal stability, increased power and energy densities, and large potential windows. Since the greatest difficulty in producing useful all-solid-state batteries comes from the comparatively low ionic conductivity of the solid electrolyte itself, many studies have been directed at the development of new highly conductive materials.[1] $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) has been shown to have a high bulk ionic conductivity (σ_b) of 1.6 $mS.cm^{-1}$ at ambient temperature.[2] It is thus one of the most promising candidates for this application.

Considerable effort has been expended to identify the structural features con-trolling the Li-ion mobility of this material over the last two decades. One characteristic of LLTO materials is that they have complex microstructures, with microdomains with different periodicities and crystal orientations.[3,4] It is likely that the high-concentration domain boundaries could act as barriers to Li-ion migration within each grain. Determination of the DB structure is thus important not only for understanding the origin of the microstructural changes with composition, but also for explaining their effect on Li-ion mobility.

In this study, based on a systematic examination of both Li-poor and Li-rich LLTO

compounds using state-of-the-art scanning transmission electron microscopy (STEM), we reveal the structures and composition of the domain boundaries (DBs) and consider their effect on Li-ion mobility and ionic conductivity, in the process positing the origin of the microstructural variations. DBs in this material are shown to consist essentially of two types: frequently occurring 90° rotation DBs and a much less common antiphase-type boundary. It is found that the 90° DBs are coherent interfaces consisting of interconnected steps that share La sites, with occupancies of La sites higher than in the domain interiors. The origin of microstructural variations in the two compounds is associated with different degrees of lattice mismatch strain at DBs in Li-poor and Li-rich materials. The lattice strain and resultant Li and O vacancies and the high La occupancy at DBs are expected to result in lower interdomain Li-ion mobility, which will have a deleterious effect on the overall Li-ion conductivity.

References

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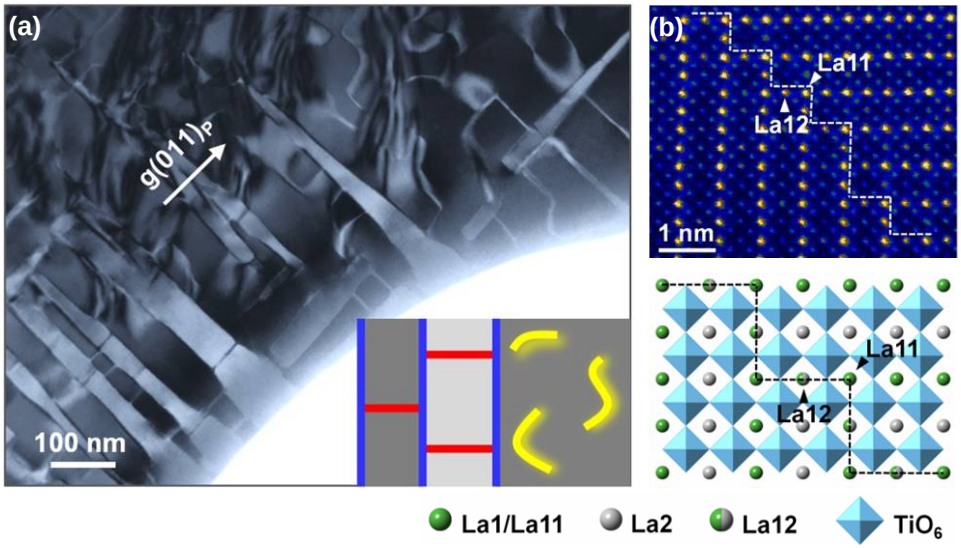

FIG. 1. (a) Low magnification two-beam bright-field TEM image showing the domain structure in Li-poor sample $La_{0.62}Li_{0.16}TiO_3$. (b) HAADF images (upper) and corresponding schematic diagrams (lower) showing the edge-on atomic structures of 90° DBs along the [100] direction. The 90° DBs are constituted of shorts steps marked by dashed lines in both cases.